Other substances which are present in wine but which are not determined as frequently as the ones discussed above can also be determined by HPLC. These include additives such as sorbic, salicylic, benzoic and ascorbic acids, which can be determined, according to OIV methods, by RP-HPLC coupled with either spectrophotometric or refractive index detectors.

Future Trends

Both GC and HPLC techniques are widely used in wine analysis. Although the methodologies are normally based on traditional separations, multidimensional chromatographic methods (with or without chiral phases) are increasingly being introduced, frequently coupled online with other analytical devices. More recently, capillary electrophoresis and supercritical fluid chromatography have also been used for wine determinations, but they are still in an early stage of application.

At present, most of the chemical compounds present in wine can be determined by means of a great variety of chromatographic methods described in the literature. Future trends, however, will focus more on internal method validation rather than on development of new methodologies. Future official methods of analysis will then include the minimum requirements (accuracy, precision, limit of detection, robustness, and so on) that an analytical method must fulfil in order to guarantee the validity of the results obtained.

See Colour Plate 128.

See also: **II / Chromatography. Extraction. II / Chromatography: Gas:** Headspace Gas Chromatography. **III / Amines:** Gas Chromatography. **Amino Acids:** Gas Chromatography; Liquid Chromatography. **Phenols:** Gas Chromatography; Liquid Chromatography; Solid-Phase Extraction.

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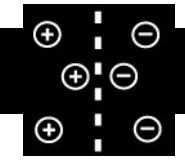
XENOBIOTICS: MAGNETIC AFFINITY SEPARATIONS

See **III / BIOLOGICALLY ACTIVE COMPOUNDS AND XENOBIOTICS: MAGNETIC AFFINITY SEPARATIONS**

ZEOLITES: ION EXCHANGERS



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The ion exchange properties of zeolites have been known since 1858, when Eichhorn studied the use of chabazite as an ion exchanger. In the 1920s and 1930s several ion exchange studies were reported.

Table 1 Phosphate based molecular sieve characteristics

Number	*Structure type*	*Porosity*	*Pore size (μm)*	*Saturation H_2O capacity ($cm^3\ g^{-1}$)*
Structure fully determined				
5	Novel	Large	0.80	0.31
11	Novel	Medium	0.60	0.16
14	Novel	Small	0.40	0.19
15	Leucophosphite			
16	Zuvnite	Very small	0.30	0.30
17	Erionite	Small	0.43	0.28
20	Sodalite	Very small	0.30	0.24
25	Novel	Very small	0.30	0.17
46	Novel			
Structures inferred from X-ray powder patterns				
37	Faujasite	Large	0.80	0.35
34	Chabazite	Small	0.43	0.30
35	Levynite	Small	0.43	0.30
42	[A]	Small	0.43	0.30
43	Gismondine	Small	0.43	0.34
44	Chabazite	Small	0.43	0.3–0.34
47	Chabazite	Small	0.43	0.3–0.34
Unknown structures				
36	Novel	Large	0.80	0.31
40	Novel	Large	0.70	0.33
31	Novel	Medium	0.65	0.17
41	Novel	Medium	0.60	0.22
18	Novel	Small	0.43	0.35
26	Novel	Small	0.43	0.23
33	Novel	Small	0.40	0.23
39	Novel	Small	0.40	0.23
28	Novel	Very small	0.30	0.21

During the 1960s many groups studied the ion exchange behaviour of the new synthetic zeolites then being produced. Due to the enormous commercial potential of zeolites, many research groups worldwide began serious efforts to sythensize new microporous zeolites and zeotype materials. The first major breakthrough was made by workers at Union Carbide, who in 1982 produced the aluminophosphate molecular sieves (**Table 1**). Although these materials are electrically neutral and have no instrinsic ion exchange properties, they did lead to the development of other substituted aluminophosphates that do have ion exchange properties (**Table 2**).

Table 2 Phosphate based molecular sieves with ion exchange character

Number	*Structure types*
40	Novel
41	Novel
34, 44	Chabazite
35	Levyne
37	Faujasite
42	A
17	Erionite
20	Sodalite
5, 11, 16, 31	$AlPO_4$

Since the early 1980s several new zeotypes, based on oxoanion frameworks, have been developed. The major group of materials of interest as far as ion exchange properties are concerned are the layered group IV acid salts. These include phosphates, arsenates, molybdates, tungstates, antimonates, silicates and silicophosphates. Most of these materials act as cation exchangers. Early attempts at synthesis mimicked zeolite preparations using reactive amorphous gels crystallized at temperatures between 120 and 200°C. This crystallization produced a variety of materials, which have been classified by their structure type: α-layered exchangers, γ-layered exchangers, fibrous exchangers, 3-D net exchangers and unsolved structure exchangers. **Table 3** lists some of the more important α-layered ion exchangers.

The structure of αZrP was determined by Clearfield in 1969. The inorganic layers are formed by a plane of octahedral Zr atoms that are linked together alternatively above and below via phosphite groups. Three oxygen atoms of the phosphite group are coordinated in this way and the fourth bears a hydrogen atom (**Figure 1**).

Table 3 Important α layered ion exchangers

Compound	*Formula*	*Interlayer distance (Å)*	*Ion exchange capacity (mmol g^{-1})*
Titanium phosphate	$Ti(HPO_4)_2 \cdot H_2O$	7.56	7.76
Zirconium phosphate	$Zr(HPO_4)_2 \cdot H_2O$	7.56	6.64
Hafnium phosphate	$Hf(HPO_4)_2 \cdot H_2O$	7.56	4.17
Germanium phosphate	$Ge(HPO_4)_2 \cdot H_2O$	7.6	7.08
Tin(IV) phosphate	$Sn(HPO_4)_2 \cdot H_2O$	7.76	6.08
Lead(IV) phosphate	$Pb(HPO_4)_2 \cdot H_2O$	7.8	4.79
Titanium arsenate	$Ti(HAsO_4)_2 \cdot H_2O$	7.77	5.78
Zirconium arsenate	$Zr(HAsO_4)_2 \cdot H_2O$	7.78	5.14
Tin(IV) arsenate	$Sn(HAsO_4)_2 \cdot H_2O$	7.8	4.80

The αZrP exchangers have been characterized by carrying out potentiometric titrations against MCl and MOH solution mixtures. X-ray analysis of the solid phases shows that αZrP is initially converted to $ZrMH(PO_4)_2 \cdot nH_2O$ then on further exchange is converted to $Zr(MPO_4)_2 \cdot nH_2O$. At any point during the ion exchange process these two phases coexist together with the solution phase. The interlayer distance is large enough to accommodate unhydrated Li^+, Na^+ and K^+; however Rb^+ and Cs^+ are too large to enter without lattice expansion. The energy to expand the lattice is supplied by a base, neutralizing the lattice protons and allowing larger cations to enter.

The γ-layered compounds are far less common than the α compounds. Both $\gamma ZrPZr(HPO_4)_2 \cdot 2H_2O$ and $\gamma TiPTi(HPO_4)_2$ are known, but both suffer from hydration at high exchange levels. Both materials have large interlayer distances and as a consequence can accept large cations such as Cs^+.

Pastor *et al*. have reviewed the synthesis, characterization and ion exchange, ion transport, sorptive and catalytic properties of inorganically pillared layered metal(IV) phosphates, typified by $Zr(BPO_4)_2 \cdot H_2O$. Porous nanostructures are generally prepared from metal(IV) phosphates either by ion exchange of polynuclear species or by intercalation from solutions of condensed species obtained by the hydrolysis of organometallic precursors using sol-gel methods. Thermal treatment is used to eliminate organic moieties, condense hydroxyl groups, eliminate water and consolidate the structure by grafting the pillar to the layer. The different strategies devised to overcome the problem presented by the high layer charge density of α- and γ-structured phosphates in obtaining porous solids are described, including exfoliation and local surface growth of pillaring ions, and modification of the zirconium phosphate matrix ix to reduce the cation exchange capacity. Structural and textural characteristics of Al, Cr, mixed Al-Cr, Fe-Cr, Ga-Al and of Si-pillared phosphates obtained from X-ray analysis by fine structure (XAFS), X-ray photoelectron spectroscopy (XPS), and magic angle spinning nuclear magnetic resonance (MAS-NMR) are presented, and the perspectives of nanocomposite pillared layered solids in general are discussed in the current context of mesoporous solids synthesized using templates.

The fibrous materials are exemplified by cerium and thorium(IV) phosphates. Their fibrous nature allows then to be fabricated into papers that allow fast separation of cations. The precise structure of these phosphates is unclear but is probably $M(HPO_4)_2 \cdot H_2O$, where M = Ce or Th.

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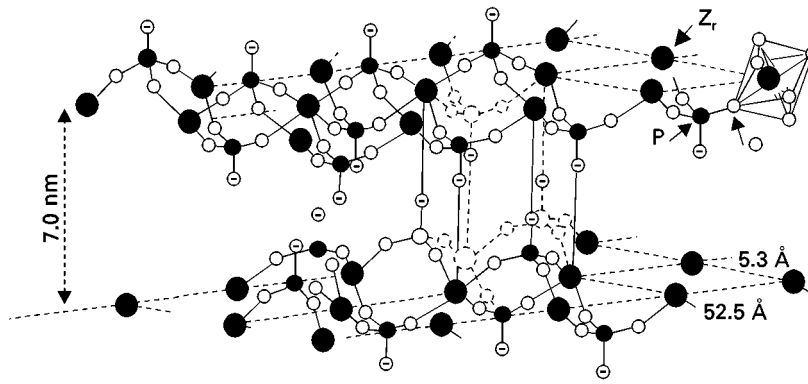

Figure 1 Structure of αZr-P.

The three-dimensional materials have the general formula $NM_2(IV)(XO_4)_3$, where M(IV) is Ti, Zr, Th or Ge; X is P or As and N is a univalent cation. The structures consist of XO_4 tetrahedra and $M(IV)O_6$ octahedral linked by corner sharing to form 3-D networks; this linking forms cavities, occupied by N^+. If phosphate is progressively replaced by silicate the cavities open up, allowing free movement of the N^+ cations and leading to the cation exchange properties. Numerous specific examples of these materials can be found in the literature, particularly the gallium phosphate-derived materials.

A more recent series of exchangers are those of the titanosilicate type, which have zeolite type pores/cavities. The materials have a formula $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$ and are synthesized from an alkaline medium under similar conditions to those used to crystallize zeolites. The structure has been solved using Rietveld refinement and shows titanium atoms in clusters of four, octahedrally coordinated by oxygen atoms. The silicate groups link the titanium clusters into a square which then shares corners with other titanium cluster squares to form a 3-D network. Half of the sodiums are linked into the framework while the other half are labile and available for ion exchange.

In 1991 a zincosilicate containing three-, four- and five-member rings connected together to form a porous eight- and intersecting nine-member ring channel was reported. Initial studies indicate that the labile monovalent cations can be exchanged.

A great deal of synthetic work has been directed at replacing the aluminium in various zeolites with other metals/nonmetals, including the crystallization of ferrisilicates, borosilicates, gallosilicates, vanadosilicates and titanosilicates. In 1992 the synthesis of a zincophosphate anionic eight-ring three-dimensional framework was reported. During the synthesis the anionic framework was stabilized by cationic, protonated diazabicyclo[2.2.2.]octane or dabco $[(H_2N_2C_6H_{12})^{2+}]$ molecules and water. These materials, although chemically similar to Clearfield's layered phosphates/phosphites, benefit from having a stable open 3-D structure. No ion exchange data has been given but thermal analysis shows that the framework is stable even after the organic dabco has been removed. This calcined material has potential as a cation exchanger. In 1991 the synthesis of sodium zirconium phosphate with a zeolite-type framework was reported. The synthesis followed typical aluminophosphate preparations using triethylamine as a template. The synthesis was carried out in an acidic medium, resulting in the template becoming protonated. Once crystalline, the sample had the template removed by calcination and the adsorption properties of the new material were studied. The material remained microporous after calcination; however, no ion exchange studies were carried out. Initial studies suggest that this material would act as a cation exchanger.

However, although an enormous number of new materials have been synthesized since 1990, there are few reports on the ion exchange characteristics of these materials.

Future Developments

Over the past five years increasing emphasis has been placed on the investigation into microporous materials based on oxoanion networks other than the aluminosilates (zeolites). The vast array of microporous materials with potential ion exchange properties is enormous. The number of reported nonzeolite molecular sieves now tops 130. The range of materials includes gallosilicates, borosilicates, ferrosilicates, germanium aluminates, titaniosilicates, silico alumino phosphate (SAPO) and metal alumino phosphate (MeAPO) molecular sieves. Most of these new materials have not yet been characterized for their ion exchange properties. The potential of these materials is as yet unrealized but, with increasing environmental demands, it is only a matter of time before these materials are explored.

See also: **II/Ion Exchange:** Historical Development; Inorganic Ion Exchangers; Novel Layered Materials: Phosphates; Novel Layered Materials: Non-Phosphates; Theory of Ion Exchange.

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ZINC ORES: FLOTATION

See **III / LEAD AND ZINC ORES: FLOTATION**

ZONE REFINING COUNTERCURRENT CHROMATOGRAPHY

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